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# Low temperature deposition of polycrystalline silicon carbide film using monomethylsilane gas

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## 1. Introduction

Silicon carbide (Greenwood and Earnshaw, 1997) has been widely used for various purposes, such as dummy wafers and reactor parts, in silicon semiconductor device production processes, due to its high purity and significantly small gas emission. In many other industries, silicon carbide has been used for coating various materials, such as carbon, in order to protect them from corrosive environment. Recently, many researchers have reported the stability of silicon carbide micro-electromechanical systems (MEMS) under corrosive conditions consisting of various chemical reagents (Mehregany et al., 2000; Stoldt et al., 2002; Rajan et al., 1999; Ashurst et al., 2004).

For producing silicon carbide film, chemical vapour deposition (CVD) is performed at the temperatures higher than 1500 K (Kimoto and Matsunami, 1994; Myers et al., 2005). Because such a high temperature is necessary, various materials having low melting point cannot be coated with silicon carbide film. Thus, the development of the low temperature silicon carbide CVD technique (Nakazawa and Suemitsu, 2000; Madapura et al., 1999) will extend and create enormous kinds of applications. For this purpose, the CVD technique using a reactive gas, such as monomethylsilane, is expected.

Here, the silicon carbide CVD using monomethylsilane gas (Habuka et al., 2007a; Habuka et al., 2009b; Habuka et al., 2010) is reviewed. In this article, first, the thermal decomposition behaviour of monomethylsilane gas is clarified. Next, the chemical reactions are designed in order to adjust the composition of silicon carbide film. Finally, silicon carbide film is obtained at low temperatures, and its stability is evaluated.

## 2. Reactor and process

The horizontal cold-wall CVD reactor shown in Figure 1 is used for obtaining a polycrystalline 3C-silicon carbide film. This reactor consists of a gas supply system, a quartz chamber and infrared lamps. The height and width of quartz chamber are 10 mm and 40 mm, respectively. A (100) silicon substrate, 30 x 40 mm, is placed on the bottom wall of the quartz chamber. The silicon substrate is heated by halogen lamps through the quartz chamber walls.

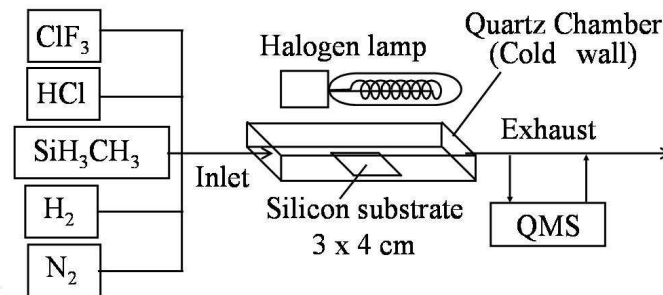


Fig. 1. Horizontal cold-wall CVD reactor for silicon carbide film deposition.

In this reactor, hydrogen gas, nitrogen gas, monomethylsilane gas, hydrogen chloride gas and chlorine trifluoride gas are used. Hydrogen is the carrier gas. It can remove the silicon oxide film and organic contamination presents at the silicon substrate surface. Hydrogen chloride gas is used for adjusting the ratio of silicon and carbon in the silicon carbide film. Throughout the deposition process, the hydrogen gas flow rate is 2 slm. Figures 2, 3 and 4 show the film deposition process, having Steps (A), (B), (C), (D) and (E).

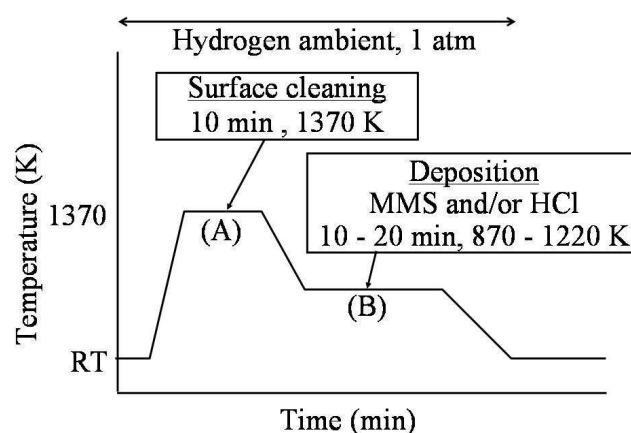


Fig. 2. Process of silicon carbide film deposition using gases of monomethylsilane, hydrogen chloride and hydrogen.

At Step (A), the silicon substrate surface is cleaned at 1370 K for 10 minutes in ambient hydrogen. Step (B) is the silicon carbide film deposition using monomethylsilane gas with or without hydrogen chloride gas at 870 - 1220 K. Step (C) is the annealing of the silicon carbide film in ambient hydrogen at 1270 K for 10 minutes.

In the process shown in Figure 2, Step (B) is performed after Step (A). In contrast to this, the process shown in Figure 3 involves first Step (A) and then the repetition of Steps (B) and (C). Figure 4 is the process for low temperature deposition and evaluation of the film, consisting of Steps (A), (D) and (E). Step (D) is the silicon carbide film deposition at low temperatures, room temperature - 1070 K, using a gas mixture of monomethylsilane and hydrogen chloride. At Step (E), the obtained film is exposed to hydrogen chloride gas at 1070 K for 10 minutes. Because hydrogen chloride gas can significantly etch silicon surface at 1070 K (Habuka et al., 2005) and does not etch silicon carbide surface, the stability of the obtained film is quickly evaluated by Step (E).

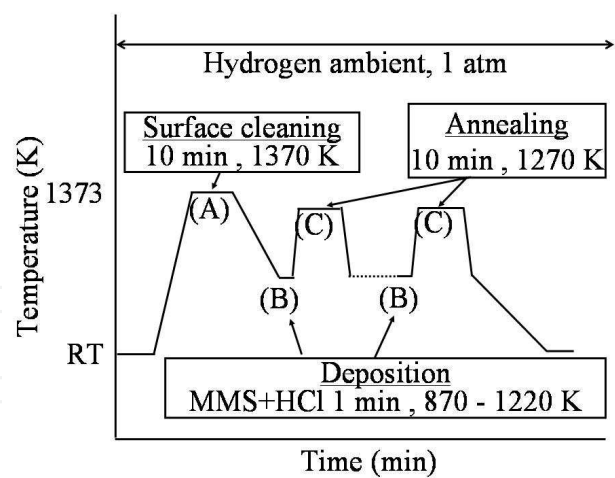


Fig. 3. Process of silicon carbide film deposition accompanying annealing step.

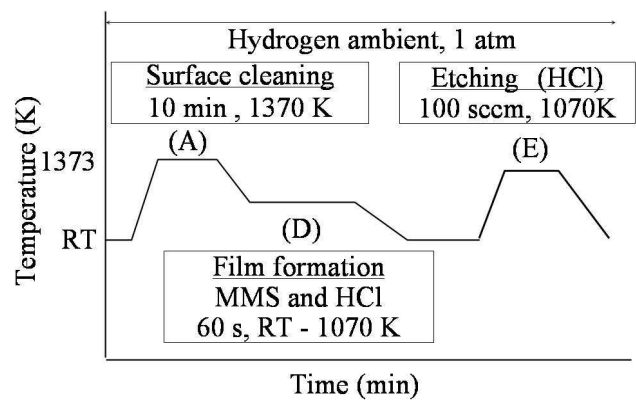


Fig. 4. Process of silicon carbide film deposition and etching.

The average thickness of the silicon carbide film is evaluated from the increase in the substrate weight. The surface morphology is observed using an optical microscope, a scanning electron microscope (SEM) and an atomic force microscope (AFM). Surface microroughness is evaluated by AFM. In order to observe the surface morphology and the film thickness, a transmission electron microscope (TEM) is used. The X-ray photoelectron spectra (XPS) reveal the chemical bonds of the silicon carbide film. Additionally, the infrared absorption spectra through the obtained film are measured.

In order to evaluate the gaseous species produced during the film deposition in the quartz chamber, a part of the exhaust gas from the reactor is fed to a quadrupole mass spectra (QMS) analyzer, as shown in Figure 1.

After finishing the film deposition, the quartz chamber is cleaned, using chlorine trifluoride gas (Kanto Denka Kogyo Co., Ltd., Tokyo, Japan) at the concentration of 10 % in ambient nitrogen at 670 - 770 K for 1 minute at atmospheric pressure.

### 3. Thermal decomposition of monomethylsilane

First, the thermal decomposition behavior of monomethylsilane gas is shown in order to choose and adjust the substrate temperature so that the silicon-carbon bond is maintained in the molecular structure during the silicon carbide film deposition.

Figure 5 shows the quadrupole mass spectra at the substrate temperatures of (a) 300 K, (b) 970 K, and (c) 1170 K. The concentration of monomethylsilane gas is 5% in ambient hydrogen at atmospheric pressure. The measured partial pressure is normalized using that of hydrogen molecule.

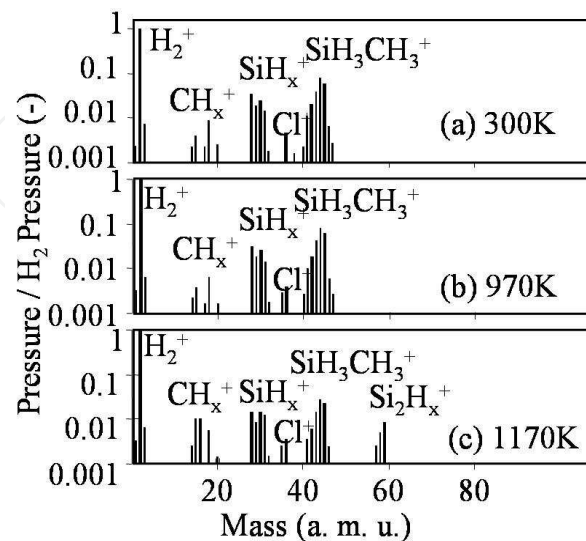


Fig. 5. Quadrupole mass spectra measured during silicon carbide film deposition at Step (B) in Figure 2. The substrate temperatures are (a) 300 K, (b) 970 K, and (c) 1170 K. The monomethylsilane concentration is 5%.

Figure 5 (a) shows the three major groups at masses greater than 12, 28 and 40 a. m. u., corresponding to  $\text{CH}_x^+$ ,  $\text{SiH}_x^+$  and  $\text{SiH}_x\text{CH}_y^+$ , respectively. Because no chemical reaction occurs at room temperature,  $\text{CH}_x^+$  and  $\text{SiH}_x^+$  are assigned to products due to the fragmentation in the mass analyzer.  $\text{Cl}^+$  is detected, as shown in Figure 5 (a), because a very small amount of chlorine from the chlorine trifluoride, used for the *in situ* cleaning, remains in the reactor. Figure 5 (b) also shows that the three major groups of  $\text{CH}_x^+$ ,  $\text{SiH}_x^+$  and  $\text{SiH}_x\text{CH}_y^+$  exist at 970 K without any significant change in their peak height compared with the spectrum in Figure 5 (a). Therefore, Figure 5 (b) indicates that the thermal decomposition of monomethylsilane gas is not significant at 970 K. However, at 1170 K, the partial pressure of the  $\text{CH}_x^+$  group increases and that of the  $\text{SiH}_x\text{CH}_y^+$  group significantly decreases, as shown in Figure 5 (c). Simultaneously, the  $\text{Si}_2\text{H}_x^+$  group appears at a mass greater than 56. The appearance of  $\text{Si}_2\text{H}_x^+$  is due to the formation of the silicon-silicon bond among  $\text{SiH}_x$  produced by the thermal decomposition of monomethylsilane.

#### 4. Film deposition from monomethylsilane

From Figure 5, a substrate temperature lower than 970 K is expected to be suitable for suppressing the thermal decomposition of monomethylsilane gas. Therefore, the silicon carbide film deposition is performed at 950 K following the process shown in Figure 2. Here, the monomethylsilane concentration is 5% in ambient hydrogen at the total flow rate of 2 slm. After the deposition, the chemical bond and the composition of the obtained film are evaluated using the XPS.

Figure 6 (a) and (b) show the XPS spectra of C 1s and Si 2p, respectively, of the film obtained from monomethylsilane gas. Because very large peaks due to the silicon-carbon bond exist near 282 eV and near 100 eV, most of the deposited film is shown to be silicon carbide. This coincides with the fact that the infrared absorption spectrum of this film showed a peak near  $793\text{ cm}^{-1}$ , which corresponds to the silicon-carbon bond (Madapura et al., 1999).

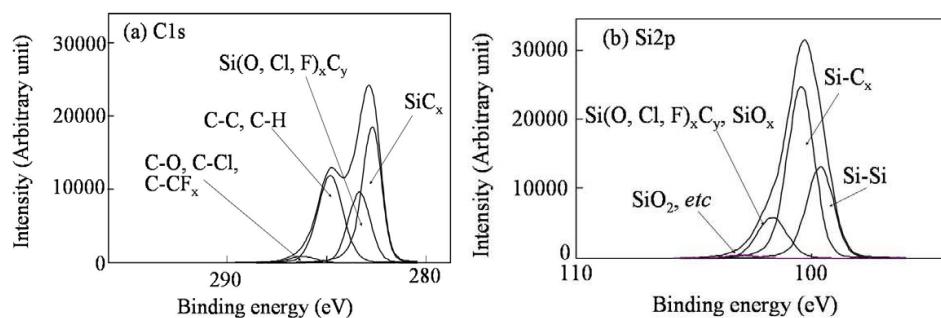


Fig. 6. XPS spectra of (a) C 1s and (b) Si 2p of silicon carbide film deposited at the monomethylsilane concentration of 5%, and at the substrate temperature of 950K.

In Figure 6, the peak corresponding to  $\text{Si}(\text{O}, \text{Cl}, \text{F})_x\text{C}_y$ ,  $\text{SiO}_x$  is detected. Because the gas mixture used for the film deposition do not include considerable amount of chlorine, and fluorine, and because the XPS measurements were performed *ex-situ*, the film surface oxidation may occur during its storage in air. This oxidation is attributed to monomethylsilane species remaining at the growth surface. The other peaks related to carbon are considered to be organic contamination on the film surface (Ishiwari et al., 2001). However, the existence of an XPS peak below 100 eV shows that this film includes a considerable amount of silicon-silicon bonds. The silicon-silicon bond can be formed due to the silicon deposition from the  $\text{SiH}_x$  produced in the gas phase. This indicates that the thermal decomposition of monomethylsilane gas in the gas phase at 950 K is not negligible, although it is significantly low at this temperature, as shown in Figure 5. Therefore, a method of reducing the excess silicon is necessary.

## 5. Film deposition from monomethylsilane and hydrogen chloride

Here, the method of reducing the excess silicon in the film is explained, adopting the process using hydrogen chloride gas shown in Figure 2.

Figure 7 shows the quadrupole mass spectrum measured during the silicon carbide film deposition using monomethylsilane gas and hydrogen chloride gas. The substrate temperature is 1090K, which is higher than 970 K used in the previous section. Because the higher temperature increases all the chemical reaction rates, any changes due to the addition of hydrogen chloride gas can be clearly recognized. At this temperature, a considerable number of silicon-carbon bonds can be maintained in monomethylsilane molecule, according to Figure 5 (c). Additionally, this temperature is near the optimum temperature for silicon carbide film growth using monomethylsilane gas, as reported by Liu and Sturm (Liu and Sturm, 1997). The gas concentrations of monomethylsilane and hydrogen chloride are 2.5% and 5%, respectively, in hydrogen gas at the flow rate of 2 slm. In Figure 7, the partial pressure of the various species is normalized using that of hydrogen molecule.



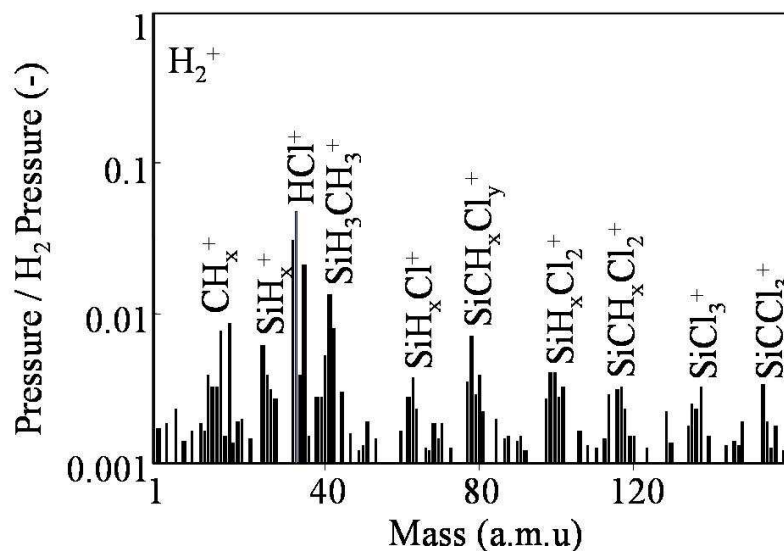


Fig. 7. Quadrupole mass spectra measured during silicon carbide film deposition by the process in Figure 2. The substrate temperature is 1090K. The monomethylsilane gas concentration is 2.3%. The hydrogen chloride gas concentration is 4.7%.

Figure 7 shows the  $\text{SiH}_x\text{CH}_y^+$ ,  $\text{CH}_x^+$ ,  $\text{SiH}_x^+$  and  $\text{HCl}^+$  groups, which are assigned to the monomethylsilane gas, its fragments and hydrogen chloride gas, respectively. In this figure, the  $\text{Si}_2\text{H}_x^+$  group was not detected, unlike Figure 5. In addition to these, there are the chlorosilane groups ( $\text{SiH}_x\text{Cl}_y$ ) at masses over 63 ( $y=1$ ), 98 ( $y=2$ ) and 133 ( $y=3$ ) and the chloromethylsilane group ( $\text{SiH}_x\text{Cl}_y\text{CH}_z$ ) at masses over 75 ( $y=1$ ), 110 ( $y=2$ ) and 145 ( $y=3$ ). Therefore, the chlorination of monomethylsilane and silanes is concluded to occur in a monomethylsilane-hydrogen chloride system.

Figure 8 (a) shows the XPS spectra of C 1s of the obtained film. The carbon-silicon bond is clearly observed at 283 eV; its oxidized or chlorinated state,  $\text{Si}(\text{O}, \text{Cl}, \text{F})_x\text{C}_y$ , also exists, as shown in this figure. The other peaks are related to the organic contamination on the film surface (Ishiwari et al., 2001). Figure 8 (b) shows the XPS spectra of Si 2p of the film obtained under the same conditions as those in the case of Figure 8 (a). Consistent with Figure 8 (a), Figure 8 (b) shows that the silicon-carbon bond and  $\text{Si}(\text{O}, \text{Cl}, \text{F})_x\text{C}_y$  bond exist on the film surface. Because the infrared absorption spectra through the obtained film showed a peak near  $793\text{ cm}^{-1}$ , which corresponded to the silicon-carbon bond (Madapura et al., 1999), most of this film is determined to be silicon carbide. From a small number of silicon-oxygen bonds in Figure 8 (b), some of the silicon-carbon bonds in the remaining intermediate species show that it has oxidized during storage in air.

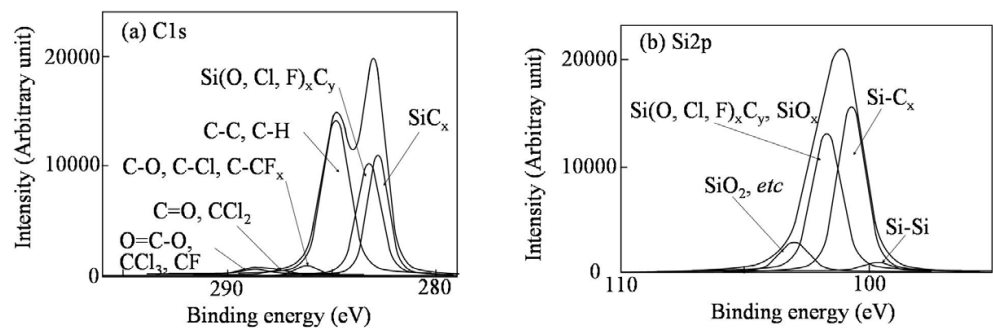


Fig. 8. XPS spectra of (a) C 1s and (b) Si 2p of silicon carbide film. The substrate temperature is 1090K. The monomethylsilane gas concentration is 2.3%. The hydrogen chloride gas concentration is 4.7%.

The most important information obtained from Figures 8 (a) and (b) is that the amount of silicon-silicon bonds are reduced at 1090 K, which is higher than that in Figure 6; many carbon-carbon bonds exist at the film surface. Therefore, this result shows that the hydrogen chloride plays a significant role in reducing the amount of excess silicon.

6. Chemical reaction in monomethylsilane and hydrogen chloride system

On the basis of the information obtained from Figures 5 – 8, the chemical reactions in the gas phase and at the substrate surface can be described as shown in Figure 9 and in Eqs. (1) – (9).

Thermal decomposition of SiH<sub>3</sub>CH<sub>3</sub>:



Si<sub>2</sub>H<sub>6</sub> production:



Si production:



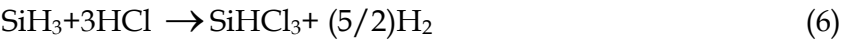
Si production:



Si etching (Habuka et al., 2005):

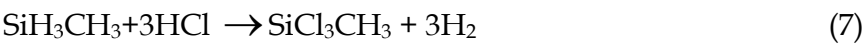


Chlorination of SiH<sub>3</sub>:

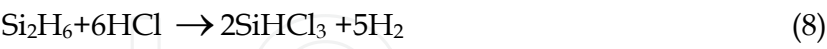




Chlorination of SiH<sub>3</sub>CH<sub>3</sub>:



Chlorination of Si<sub>2</sub>H<sub>6</sub>:



Silicon carbide production:

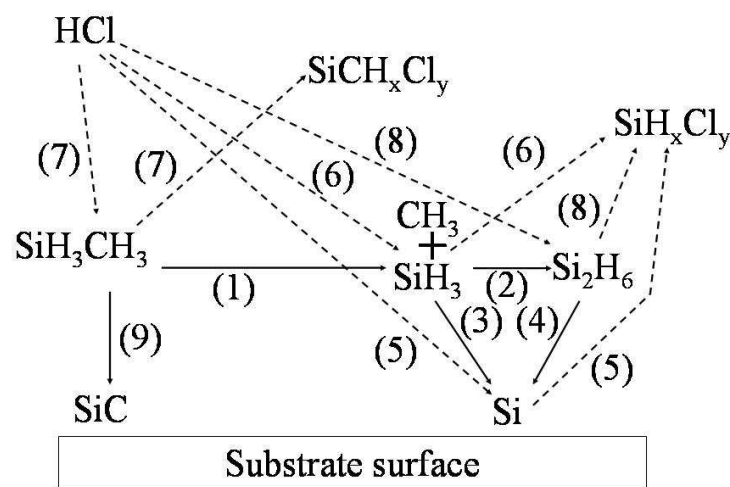


Fig. 9. Chemical process of silicon carbide film deposition using monomethylsilane gas and hydrogen chloride gas. (i) is the equation number.

In these chemical reactions, a small amount of monomethylsilane gas is thermally decomposed to form SiH<sub>3</sub>, as shown by Eq. (1). SiH<sub>3</sub> forms silicon-silicon chemical bonds with each other to produce Si<sub>2</sub>H<sub>6</sub> following Eq. (2). Both SiH<sub>3</sub> and Si<sub>2</sub>H<sub>6</sub> can produce silicon in the gas phase and at the substrate surface, following Eqs. (3) and (4), respectively. One of the possible origins of chlorosilanes, as shown in Figure 7, is the etching of silicon at the substrate surface, as described in Eq. (5), because the silicon etch rate using hydrogen chloride is considerably high (Habuka et al., 2005). Another reason for the production of chlorosilanes is the chemical reaction of hydrogen chloride gas with SiH<sub>3</sub> and Si<sub>2</sub>H<sub>6</sub> in the gas phase, as described in Eqs. (6) and (8), respectively. Because chloromethylsilanes are simultaneously detected, monomethylsilane reacts with hydrogen chloride, as shown in Eq. (7). In addition to these reactions, silicon carbide is produced by the chemical reaction in Eq. (9).

The chemical reactions, Eqs. (1) - (8), can affect the film composition. Si<sub>2</sub>H<sub>x</sub> is very easily decomposed to produce silicon clusters in the gas phase and on the substrate surface, in Eq. (4). However, the formation of Si<sub>2</sub>H<sub>6</sub> is suppressed by means of the production of SiHCl<sub>3</sub> from SiH<sub>3</sub>, in Eq. (6), immediately after the SiH<sub>3</sub> formation. Therefore, the number of silicon clusters produced in the gas phase is reduced by adding the hydrogen chloride gas; this change can affect the composition of the film.

Here, the composition of the film measured by XPS shows that the film surface formed without using hydrogen chloride gas has greater silicon content than that of carbon, as shown in Figure 6. In contrast, the film surface obtained using hydrogen chloride gas has a smaller silicon content than that of carbon, as shown in Figure 8. This result shows that hydrogen chloride gas can reduce the excess silicon on the film surface; the film composition can be adjusted by changing the ratio of hydrogen chloride gas to monomethylsilane gas.

## 7. Film thickness

Figure 10 shows the relationship between the silicon carbide film thickness and the deposition time, using the process shown in Figure 2, at the substrate temperature of 1070 K. As shown in this figure, the film thickness is maintained at around 0.14  $\mu\text{m}$  from 1 to 30 minutes. This shows that the film deposition stops within 1 minute. This coincides with those obtained by Ikoma et al. (Ikoma., 1999) and Boo et al. (Boo et al, 1999) using monomethylsilane gas.

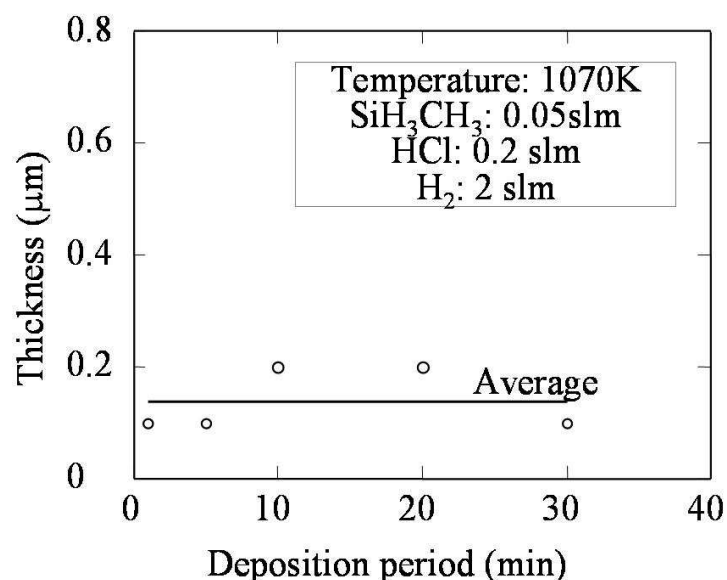


Fig. 10. Relationship between silicon carbide film thickness and deposition period, at the substrate temperature of 1070 K. The flow rate of monomethylsilane and hydrogen chloride is 0.05 slm and 0.2 slm, respectively, in hydrogen gas of 2 slm.

When the deposition stopped, the surface is assumed to have a major amount of carbon terminated with hydrogen. This assumption is consistent with the following results:

- (1) The bonding energy between carbon and hydrogen is much higher than that of other chemical bonds among silicon, hydrogen and chlorine (Kagaku Binran, 1984).
- (2) Hydrogen bonded with carbon remains at temperatures less than 1270 K (Nakazawa and Suemitsu, 2000).
- (3) The silicon-hydrogen and silicon-chlorine chemical bonds cannot perfectly terminate the surface to stop the film deposition, because the silicon epitaxial film growth can continue in a chlorosilane-hydrogen system at 1070 K (Habuka et al., 1996).

In order to remove the hydrogen atoms bonded with carbon at the surface, high-temperature annealing is convenient. Using the process shown in Figure 3, the substrate is heated at 1270 K for 10 minutes, Step (C), before and after the film deposition at 1070 K. Here, the film deposition period in each step is 1 minute.

Figure 11 shows the thickness of silicon carbide film obtained by the process employing Step (C), between the film deposition steps, as shown in Figure 3. The flow rates of hydrogen gas and hydrogen chloride gas are fixed to 2 slm and 0.2 slm, respectively. The flow rate of monomethylsilane gas is 0.05 and 0.1 slm. The film deposition period at each step is 1 minute. The film thickness increases with the increasing flow rate of monomethylsilane gas. Simultaneously, the film thickness is increased by repeating the deposition and annealing. The thickness of the obtained film is greater than 2  $\mu\text{m}$  with the total deposition period of 4 minutes.

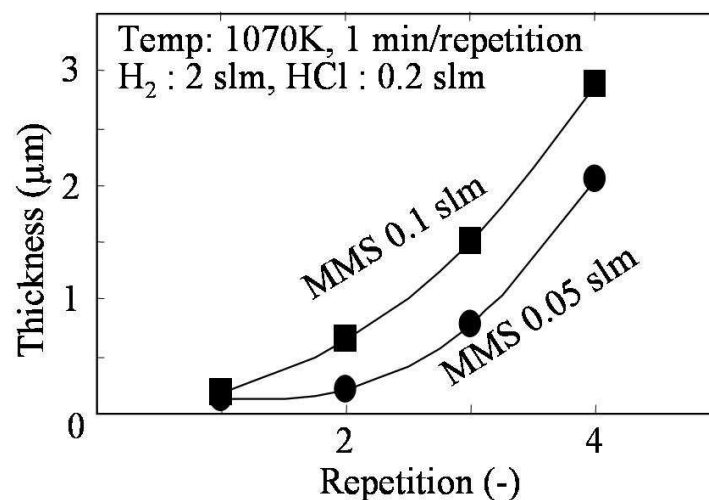


Fig. 11. Silicon carbide film thickness increasing with the repetition of the deposition using monomethylsilane gas with hydrogen chloride gas (Step (B)) at 1070 K and the annealing at 1270 K (Step (C)). The flow rate of monomethylsilane gas is 0.05 slm and 0.1 slm. The flow rate of hydrogen chloride and hydrogen is 0.2 slm and 2 slm, respectively.

Figure 12 shows the infrared spectra of the films corresponding to those at the monomethylsilane gas flow rate of 0.05 slm in Figure 11. The numbers in this figure indicate the number of repetitions of Steps (B) and (C) in Figure 3. Although these spectra are very noisy, a change in the transmittance clearly appears at the silicon carbide reststrahl band (700 - 900  $\text{cm}^{-1}$ ) (MacMillan et al., 1996). With the increasing number of repetitions of Steps (B) and (C), the transmittance near 793  $\text{cm}^{-1}$  of 3C-silicon carbide (Madapura et al., 1999) significantly decreases while maintaining the wave-number having a very wide absorption bandwidth. Therefore, the thick film obtained by the process shown in Figure 3 is polycrystalline 3C-silicon carbide.

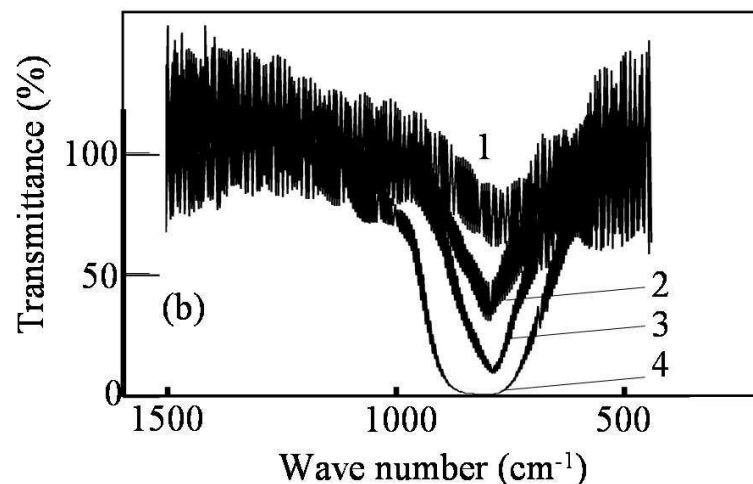


Fig. 12. Infrared absorption spectra of silicon carbide film after repeatedly supplying gas mixture of monomethylsilane and hydrogen chloride for 1 min at 1070 K (Step (B)) and annealing at 1270 K for 10 min (Step (C)). The flow rates of monomethylsilane and hydrogen chloride are 0.05 slm and 0.2 slm, respectively, in hydrogen gas of 2 slm.

Figures 13 and 14 show the surface of the film obtained at 1070K, corresponding to 4 repetitions of Steps (B) and (C) in Figures 11 and 12. The substrate surface is covered with the film having small grains, and it has neither porous nor needle-like appearance.

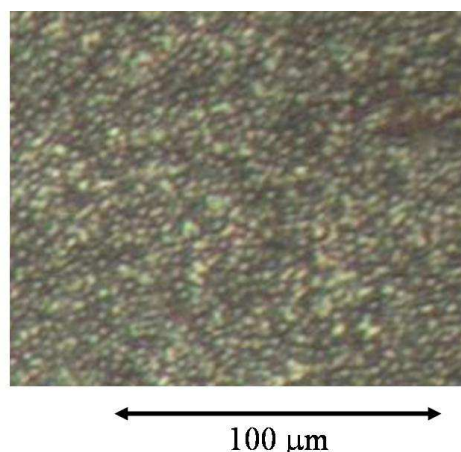


Fig. 13. Surface morphology of the silicon carbide film after four repetitions of Steps (B) and (C), observed using optical microscope. The condition of silicon carbide film is the same as that in Figure 12.

Figure 15 shows the morphology of the film surface which is obtained after (R1) one, (R2) two, (R3) three and (R4) four repetitions of Steps (B) and (C). At the deposition, substrate temperature is 1070 K; the flow rate of monomethylsilane gas is 0.05 slm. The flow rate of hydrogen chloride and hydrogen is 0.2 slm and 2 slm, respectively. With increasing the repetitions, the film surface tends to be slightly rough, and shows very small grains. However, no significant roughening is recognized to occur.

When the film deposition is governed by particles formed in the gas phase, the film deposition can continue as long as the monomethylsilane gas is supplied. However, the film

deposition saturated. Therefore, the film having the small grain appearance is concluded to be formed dominantly by the surface process. Additionally, it is noted here that the roughening of silicon substrate surface due to etching by hydrogen chloride is not significant, because the film surface can be covered with silicon carbide, immediately after initiating the film deposition.

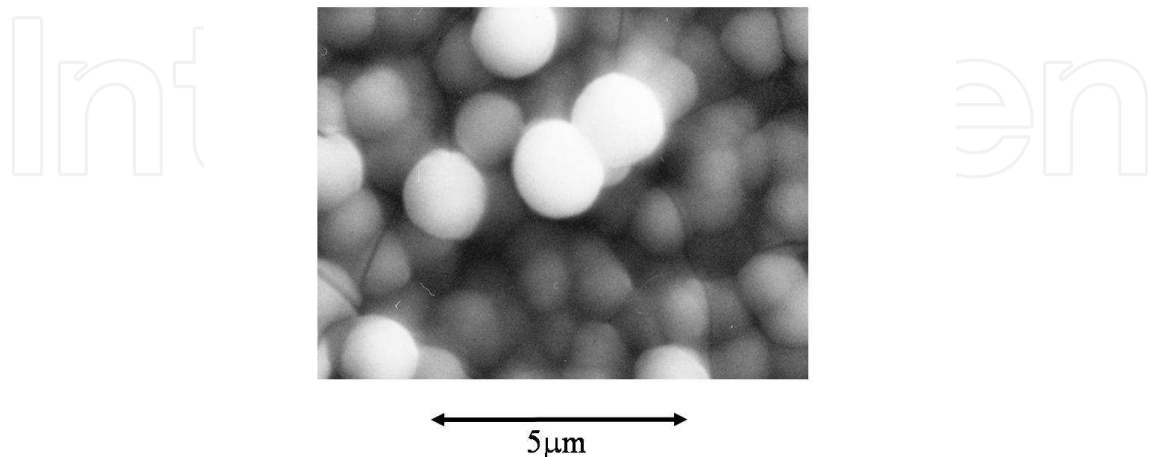


Fig. 14. SEM image of the film surface after four repetitions of Steps (B) and (C). The condition of silicon carbide film is the same as that in Figure 12.

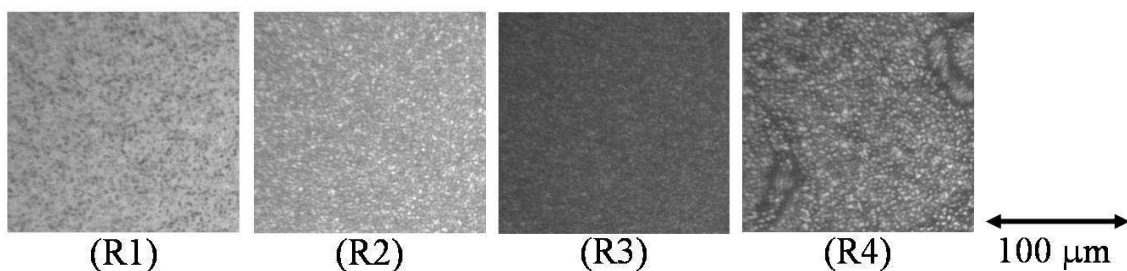


Fig. 15. Photograph of the silicon carbide film surface, obtained at 1070 K and at monomethylsilane gas flow rate of 0.05 slm. The flow rate of hydrogen chloride and hydrogen is 0.2 slm and 2 slm, respectively. (R1), (R2), (R3) and (R4) are obtained after one, two, three and four repetitions, respectively, of Steps (B) and (C) in Figure 3.

## 9. Surface chemical process: stop and restart deposition

The surface chemical process is discussed in relation to stopping and restarting the silicon carbide film growth.

The silicon carbide film deposition starts at the silicon substrate surface, as shown in Figure 16 (i). During Step (B) in Figure 3, silicon carbide film is formed, as shown in Figure 16 (ii). However, because the carbon-hydrogen bond tends to remain (Nakazawa and Suemitsu, 2000; Yoon et al., 2000), carbon at the surface can be terminated with hydrogen, as shown in Figure 16 (iii).

The hydrogen terminating the silicon carbide film surface is removed by means of high temperature annealing, as shown in Figure 16 (iv). Here, the bare silicon carbide surface can be formed; the process can return to the surface shown in Figure 16 (ii), at which Step (B) is possible.



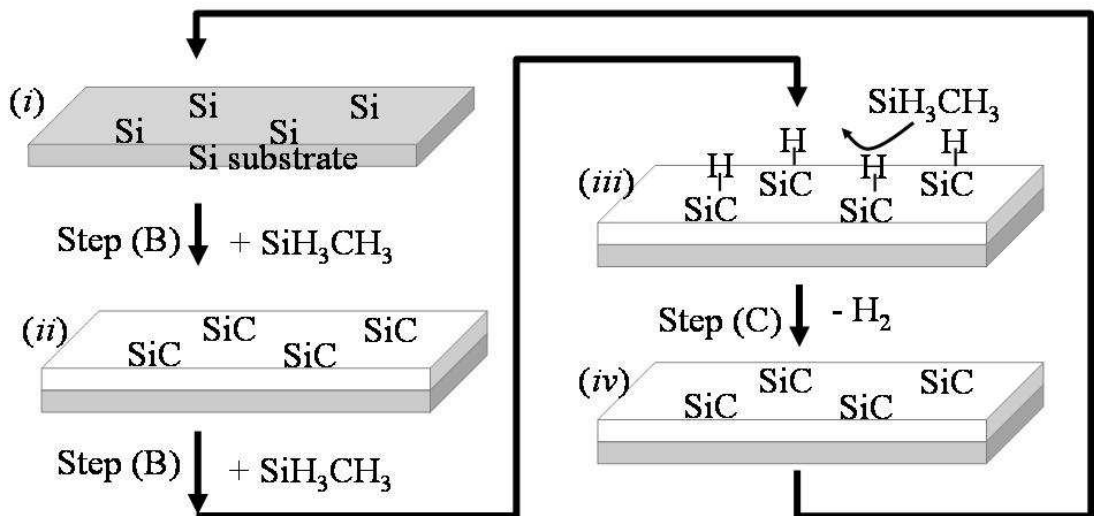


Fig. 16. Chemical process for silicon carbide film formation from monomethylsilane gas. (i): silicon substrate, (ii): silicon carbide deposition using monomethylsilane gas, (iii): surface termination by hydrogen, and (iv): desorption of hydrogen.

The effective method to increase the film thickness, other than the repetition of Steps (B) and (C), is to increase the growth rate at Step (B), while the hydrogen-terminated surface is built. Figure 11 shows that the obtained film thickness at the monomethylsilane gas flow rate of 0.1 slm is greater than that at 0.05 slm. Thus, the silicon carbide film growth rate increases with the monomethylsilane gas concentration.

## 10. Hydrogen chloride gas flow rate

The silicon carbide film thickness at various gas compositions of monomethylsilane and hydrogen chloride for 5 minutes at 1070 K is shown in Figure 17. The hydrogen gas flow rate is 2 slm; the hydrogen chloride gas flow rate is 0.1 slm (circle), 0.15 slm (square) and 0.2 slm (triangle).

In Figure 17, the film thickness entirely decreases with the increasing hydrogen chloride gas flow rate. The square and triangle show that the silicon carbide film thickness is very small but it gradually increases with the increasing monomethylsilane gas flow rate between 0.05 and 0.2 slm. In contrast to this, the silicon carbide film thickness obtained at the hydrogen chloride gas flow rate of 0.1 slm, indicated by the circle, shows a significant increase at the monomethylsilane gas flow rate greater than 0.1 slm. Simultaneously, the surface appearance of the film having such a significant thickness increase becomes dark and very rough.



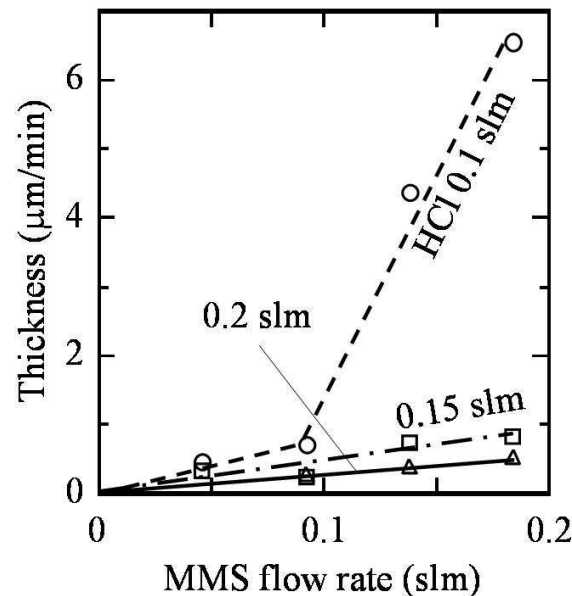


Fig. 17. Silicon carbide film thickness produced for 1 minute at 1070 K. Hydrogen chloride gas flow rate is 0.1 slm (circle), 0.15 slm (square) and 0.2 slm (triangle). Hydrogen gas flow rate is 2 slm.

Here, it should be noted that the silicon substrate surface was significantly etched by hydrogen chloride gas at its flow rate of 0.1 slm for 60 s, without monomethylsilane gas. This indicates that the silicon-silicon bond present at the film surface can be removed by hydrogen chloride gas. Thus, from these results, the amount of excess silicon in the silicon carbide film is decreased, however, the insufficient amount of hydrogen chloride gas can not sufficiently suppress the incorporation of excess silicon. From Figure 17, the amount of hydrogen chloride gas, comparable to or greater than that of the monomethylsilane gas, is necessary for the effective removal of the excess silicon. Because the hydrogen chloride flow rate larger than 0.15 slm is sufficient for the film formation at the monomethylsilane gas flow rate between 0.05 and 0.2 slm, the film thickness could linearly increase with the increasing monomethylsilane gas flow rate, as indicated using square and triangle in Figure 17.

## 11. Surface morphology

The surface morphology of the silicon carbide film is evaluated by the AFM, because some of the silicon carbide films obtained from monomethylsilane gas shows a mirror-like appearance by visual inspection. Figure 18 shows the AFM photograph of (a) silicon surface before the film formation, and (b) silicon carbide film surface with a thickness of 0.2 μm obtained at 1070 K for 5 min at the monomethylsilane gas flow rate of 0.092 slm and hydrogen chloride gas flow rate of 0.15 slm. The measured area was 0.2 × 0.2 μm.

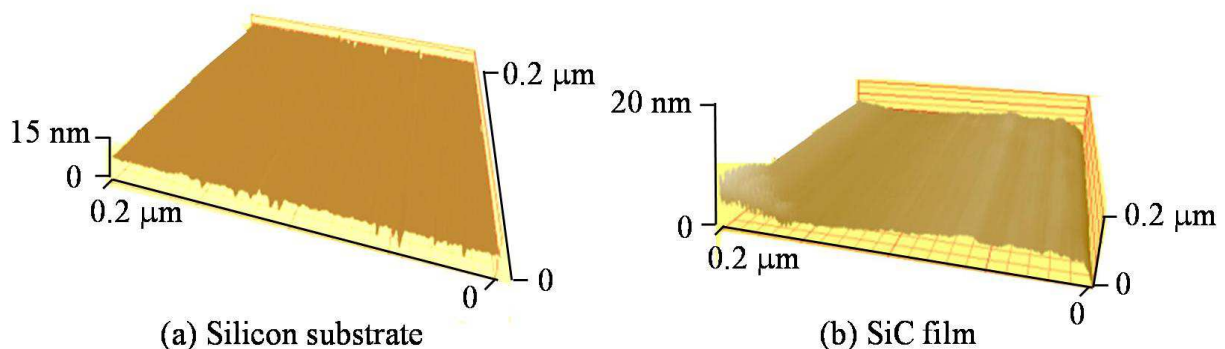


Fig. 18. AFM photograph of (a) silicon substrate surface and (b) silicon carbide film surface with the thickness of  $0.2\ \mu\text{m}$  obtained at  $1070\ \text{K}$  for 5 minutes at the monomethylsilane gas flow rate of  $0.092\ \text{slm}$  and hydrogen chloride gas flow rate of  $0.15\ \text{slm}$ . The Ra and RMS microroughness are  $0.6\ \text{nm}$  and  $0.7\ \text{nm}$ , respectively.

Figure 18 (a) shows that the silicon substrate surface before the film formation is very smooth with the average roughness (Ra) and the root-mean-square roughness (RMS) of  $0.2\ \text{nm}$  and  $0.3\ \text{nm}$ , respectively. After the silicon carbide film formation, the surface roughness slightly increases due to the formation of short hillocks, as shown in Figure 18 (b). However, its surface appearance is still specular by visual inspection. The Ra and RMS microroughness are  $0.6\ \text{nm}$  and  $0.7\ \text{nm}$ , respectively.

Some of the silicon carbide films obtained from monomethylsilane gas at  $1070\ \text{K}$  show a small grain-like surface, as shown in Figures 13, 14 and 15, but the other films often show a specular surface. Because the specular surface is expected to have a higher coating quality than that of a grain-like surface, the condition for obtaining the smooth surface with a high reproducibility should be studied in future.

## 12. Low temperature deposition

In this section, the low temperature silicon carbide film formation is described. For maintaining the gas condition in a series of film deposition, hydrogen chloride gas is introduced with monomethylsilane gas, even at room temperature, at which temperature hydrogen chloride gas hardly reacts with silicon. In the silicon carbide film formation for 60 seconds at various temperatures between  $1070\ \text{K}$  and room temperature following Steps (A) and (D) in Figure 4, the obtained film thickness was around  $0.1\ \mu\text{m}$ , and their surface often has a grain-like morphology, as shown in Figure 19 and a yellowish appearance indicating the existence of the silicon carbide film. Thus, the film formation at the lowest temperature, that is, at room temperature, is further explained.

The average film thickness obtained at room temperature, following Steps (A) and (D) in Figure 4, is  $0.1\ \mu\text{m}$ , which is comparable to the thickness obtained at  $1070\ \text{K}$ . In order to quickly evaluate the coating quality of the silicon carbide film, the film surface is further exposed to hydrogen chloride gas at  $1070\ \text{K}$ , following Step (E) in Figure 4. Because the film shows no decrease in weight and no change in its surface appearance, the film formed at room temperature is expected to be silicon carbide.

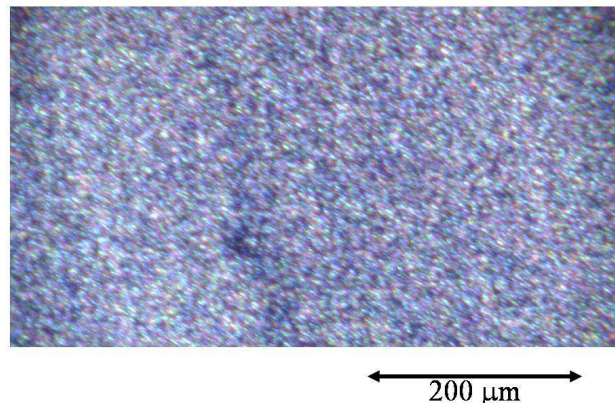


Fig. 19. Surface morphology of the film formed at room temperature for 60 s using monomethylsilane gas (0.092 slm) and hydrogen chloride gas (0.15 slm), immediately after the surface cleaning in ambient hydrogen at 1370 K for 10 min.

In order to show the necessary condition for the film formation at room temperature, monomethylsilane gas is supplied to silicon substrate skipping the silicon surface cleaning (Step (A)) of the process shown in Figure 4. This resulted in no weight increase to indicate no film formation; its surface was significantly etched by hydrogen chloride gas at 1070 K, by Step (E) in Figure 4. Thus, the surface cleaning in ambient hydrogen (Step (A)) takes an important role for the silicon carbide film formation from monomethylsilane gas at low temperatures.

In order to verify the silicon carbide film formation, Figure 20 shows the XPS spectra of C 1s of the 0.1 μm-thick deposited film which is obtained from monomethylsilane gas at room temperature, and further etched by hydrogen chloride gas at 1070 K for 10 minutes, following Steps (A), (D) and (E) shown in Figure 4. Figure 20 clearly shows the existence of the Si-C bond at 283 eV. Because silicon atom bonding with the carbon atom is consistently detected at 101 eV, the obtained film contains the Si-C bond.

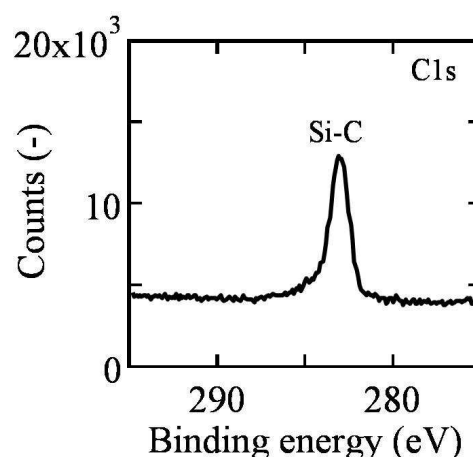


Fig. 20. XPS spectra of C1s of the silicon carbide film, obtained from monomethylsilane gas and hydrogen chloride gas on silicon surface at room temperature after annealing in hydrogen ambient. This film was further exposed to hydrogen chloride gas at 1070 K for 10 min before the XPS measurement.

### 13. Stability of film

In order to evaluate the stability of the silicon carbide film formed at room temperature, the obtained film is exposed to hydrogen chloride gas at 1070 K, following Step (C) in Figure 4; its surface is compared with that of a silicon substrate after exposed to hydrogen chloride gas.

Figure 21 shows SEM photograph of the silicon substrate surface and silicon carbide film. Figure 21 (a) is the silicon substrate surface after etching using hydrogen chloride gas at the flow rate of 0.1 slm diluted by hydrogen gas of 2 slm, at the substrate temperature of 1070 K for 10 min, without silicon carbide film formation. This figure shows the existence of many pits indicating the occurrence of etching by hydrogen chloride gas.

Figure 21 (b) shows the silicon carbide film surface formed using monomethylsilane gas of 0.069 slm at room temperature for 1 minute. This figure shows that there is no large pit at the film surface. Next, this surface is exposed to hydrogen chloride gas at the flow rate of 0.1 slm diluted in hydrogen gas of 2 slm, at 1070 K for 10 min. This condition is exactly the same as that performed for the silicon surface, shown in Fig. 21 (a). As shown in Figure 21 (c), a considerable morphology change is not observed at the deposited film surface, except of particles intentionally taken in order to clearly focus the surface for SEM observation.

Figure 22 is the TEM micrograph of the cross section of the silicon carbide film. The film, shown in this figure, was obtained from monomethylsilane gas and hydrogen chloride gas on silicon surface at room temperature after annealing at 1370 K in hydrogen ambient. This film was further exposed to hydrogen chloride gas at 1070 K for 10 min, before the TEM measurement.

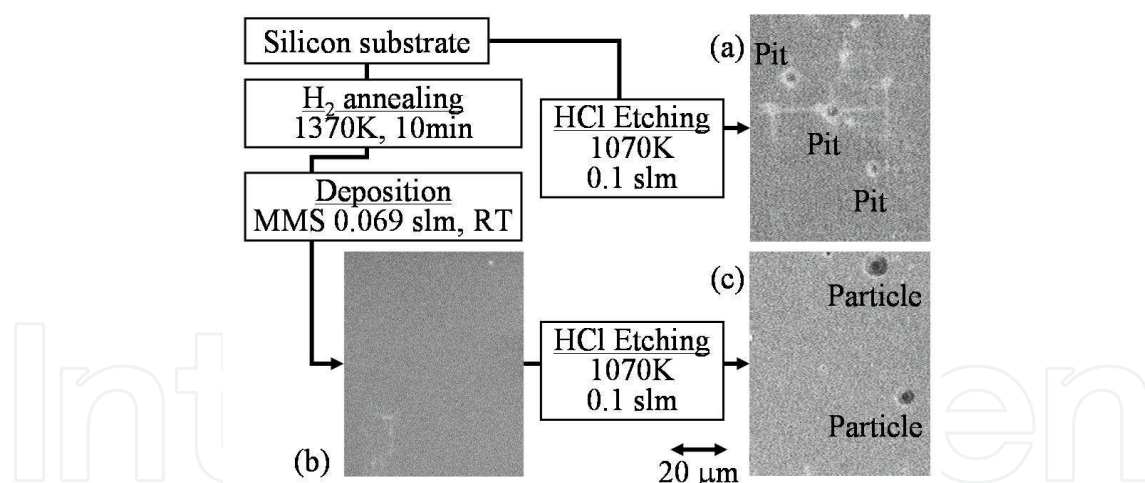


Fig. 21. Surface of (a) silicon substrate after etching using hydrogen chloride gas at 1070 K for 10 min, (b) deposited film using monomethylsilane gas of 0.069 slm at room temperature, and (c) the film of (b) further etched using hydrogen chloride gas at 1070 K for 10 min.

Figure 22 shows that the entire silicon substrate surface is sufficiently covered with the silicon carbide film consisted of arranged many grains, diameter of which is about 0.2 – 0.3  $\mu\text{m}$ . The average film thickness in the observed area is about 0.3  $\mu\text{m}$ . Additionally, there are no etch pit and pin-hole caused due to etching by hydrogen chloride gas at the silicon carbide-silicon interface. Thus, the silicon carbide film deposited at room temperature is stable in a hazardous ambient including hydrogen chloride gas.

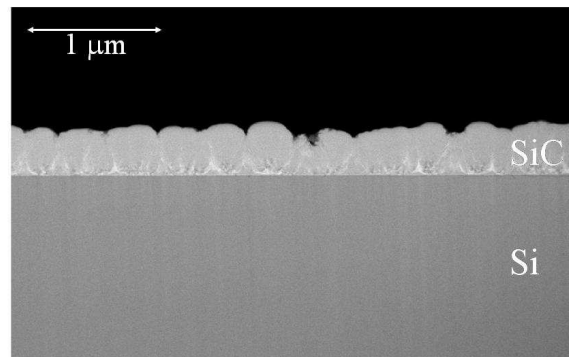


Fig. 22. TEM micrograph of the cross section of the silicon carbide film, shown in Figure 21 (c).

#### 14. Film formation mechanism at room temperature

Based on the result that the surface cleaning in ambient hydrogen is necessary for producing the silicon carbide film, the surface chemical process for the low temperature silicon carbide formation using monomethylsilane gas is shown Figure 23.

The silicon carbide film formation is initiated by Step (i), as shown in Figure 23. At Step (i), monomethylsilane molecule approaches to silicon dimer present at hydrogen-terminated silicon surface. The silicon dimer is assumed to be broken in order to accept monomethylsilane molecule. Here, Step (i) is for an initiation of the surface chemical reaction; Steps (ii) and (iii) are for a repetition of the surface chemical reaction to produce multilayer film. After Step (i), Processes 1, 2 and 3, are expected to occur.

At Step (ii) in Process 1, silicon atom in monomethylsilane forms covalent bonds with silicon atom of the substrate. Here, hydrogen radicals are produced. The hydrogen radicals bond to the neighboring silicon atoms. At Step (iii) in Process 1, two hydrogen atoms are produced; dangling bonds remain at the neighboring silicon atoms.

At Step (ii) in Process 2, silicon atom in monomethylsilane forms covalent bonds with silicon atom of the substrate, similar to Process 1. Next, one of the hydrogen radicals produced can approach the hydrogen atom bonding with the carbon atoms in the chemisorbed monomethylsilane molecule. At Step (iii) in Process 2, two hydrogen atoms are produced; dangling bonds remain at the neighboring silicon atom and at the carbon atom in the monomethylsilane.

At Step (ii) in Process 3, silicon atom in monomethylsilane forms covalent bonds with silicon atom of the substrate, similar to Processes 1 and 2; one of the hydrogen radical produced can approach the hydrogen atom bonding with the silicon atom in the chemisorbed monomethylsilane molecule. At Step (iii) in Process 3, two hydrogen atoms are produced; dangling bonds remain at the neighboring silicon atom and at the silicon atom in the monomethylsilane. Because the dangling bonds formed after Step (iii) of Processes 1, 2 and 3, can accept more monomethylsilane molecules, chemisorption of monomethylsilane is expected to be spread and repeated over the substrate surface.



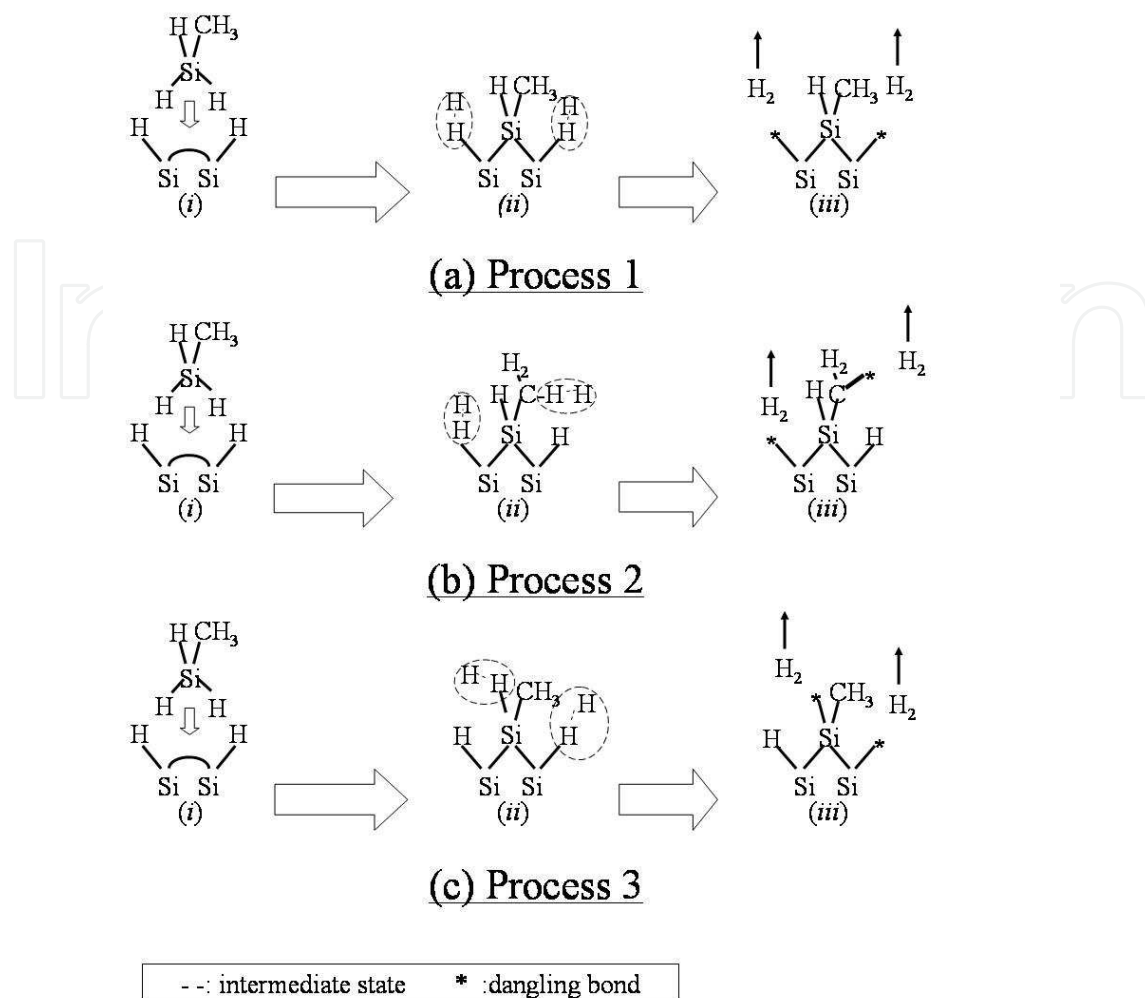


Fig. 23. Surface processes 1, 2 and 3 for low temperature silicon carbide film growth. (i) approach of monomethylsilane to silicon dimer at hydrogen-terminated silicon surface, (ii) chemisorption of monomethylsilane and production of hydrogen radicals, and (iii) production of hydrogen molecules, and dangling bonds.

When Process 2 is slower than Process 3, a larger amount of C-H bond remains at the film surface. Because this induces the C-H termination over the entire surface, the silicon carbide film formation finally stops.

Here, silicon dimer was reported to be very weak (Redondo and Goddard III, 1982); many research groups (Nakazawa and Suemitsu, 2000; Sutherland et al., 1997) reported the occurrence of the dissociative adsorption of organosilane on silicon dimer at room temperature. Additionally, Silvestrelli et al. (Silvestrelli et al., 2003) reported that  $\text{SiH}_2\text{CH}_3$  can bond to silicon dimer, when monomethylsilane molecule vertically approached the surface. Taking into account these previous studies, the surface process, shown in Figure 23, is consistent with the results of the low temperature silicon carbide film formation and its saturation, using monomethylsilane gas.



## 15. Reactor cleaning using chlorine trifluoride gas

During the film deposition, the silicon carbide film is very often formed at various positions in the reactor other than the substrate. Particularly, the susceptor suffers significant deposition. When such a film becomes thick, small particles are produced from the film and they attach at the film surface. This behaviour causes the quality deterioration of film surface. Thus, the susceptor and the inner wall of the reactor should be cleaned after each deposition.

Because silicon carbide is very stable material, as shown in Figure 21 (c), the cleaning of the silicon carbide CVD reactor is quite difficult, except when using chlorine trifluoride gas (Habuka et al., 2009).

Figure 24 (a) shows the quartz chamber which has a thick dark-brown-coloured film formed at its inner surface. Because this thick film was formed from monomethylsilane gas at the substrate temperature of higher than 1000 K, it is a mixture of silicon carbide and silicon.

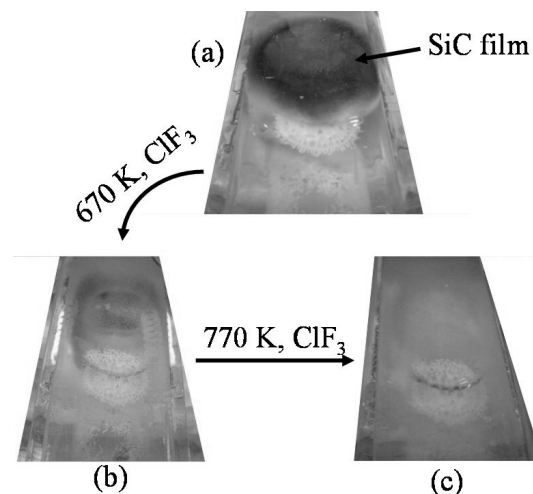


Fig. 24. Photograph of quartz chamber (a) after silicon carbide film deposition using monomethylsilane gas at high temperatures, (b) after cleaning using chlorine trifluoride gas at 10% in ambient nitrogen and at 670 K, and (c) after cleaning using chlorine trifluoride gas at 10% and 770 K.

Most of the deposited film is removed by chlorine trifluoride at its concentration of 10% gas at 670 K, as shown in Figure 24 (b), within 5 minutes, although very small amount of silicon carbide film remains. The remained film was removed again using chlorine trifluoride gas at 10 % and at 770 K, as shown in Figure 24 (c). Because very slight etching of quartz glass occurs, the cleaning condition has been discussed by Miura et al. (Miura et al., 2009).

## 16. Conclusions

The 3C-silicon carbide thin film is formed on silicon surface using monomethylsilane gas at the temperatures between room temperature and 1270 K. Although silicon, produced by thermal decomposition in gas phase and substrate surface, is incorporated into the silicon carbide film, it can be significantly reduced by means of the addition of hydrogen chloride gas. Although the silicon carbide film formation saturates within 1 minute due to the surface termination by C-H bonds, it can start again by means of annealing at 1270 K for removing

hydrogen atoms. In order to develop the low-temperature silicon carbide film formation process, monomethylsilane gas is introduced to silicon substrate at room temperature. After the silicon surface is cleaned at 1370 K and cooled down in hydrogen ambient, monomethylsilane molecule can adsorb on the silicon surface to produce silicon carbide film, even at room temperature. Such the low temperature film formation is possible, because the hydrogen terminated silicon surface has silicon dimer. The silicon carbide film formed at room temperature is shown to be stable, because it can maintain after the etching using hydrogen chloride gas at 1070 K.

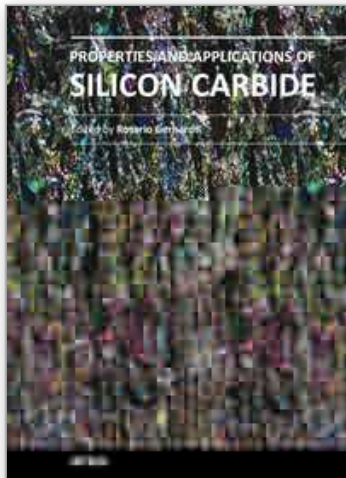
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## **Properties and Applications of Silicon Carbide**

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In this book, we explore an eclectic mix of articles that highlight some new potential applications of SiC and different ways to achieve specific properties. Some articles describe well-established processing methods, while others highlight phase equilibria or machining methods. A resurgence of interest in the structural arena is evident, while new ways to utilize the interesting electromagnetic properties of SiC continue to increase.

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